

# Modeling transport of dissolved silica in a forested headwater catchment: Implications for defining the hydrochemical response of observed flow pathways

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**Abstract.** Groundwater, subsurface stormflow, and overland flow components of discharge, derived from a hydrological model that was applied to a forested headwater catchment in north central Virginia, were used with measured stream water and lysimeter concentrations of dissolved silica to investigate the hydrochemical behavior of the catchment. Concentrations in base flow, taken to be a reflection of groundwater, vary with discharge, an observation in conflict with the typical assumption of constant concentration used in end-member mixing analyses. This observed flow dependence was modeled by considering the concentration in groundwater to be related to the saturation deficit in this zone. A positive correlation between the average groundwater saturation deficit and base flow dissolved silica concentrations is consistent with batch experiments and petrographic analysis of regolith core samples, which both indicate an increase in silica available for dissolution with depth in the groundwater zone. In the absence of subsurface storm flow zone sampling during rainfall events a constant concentration was assumed for this zone. Concentration-discharge (C-Q) paths in the stream were used to evaluate the modeled stream silica concentrations. An inconsistency in the direction of the modeled C-Q rotations suggests that the storm flow zone dissolved silica concentration may also vary with time, because of the “flushing” of high-concentration, preevent soil water on the rising limb of the storm hydrograph. For this catchment in Virginia the assumption of a constant concentration for subsurface storm flow, as well as for base flow, appears to be invalid.

## 1. Introduction

Much attention has been paid in the recent literature to isotopic and geochemical hydrograph separation methods for identifying catchment processes involved in acid deposition, chemical weathering, and contaminant transport. The validity of these techniques rests upon the accurate conceptualization of the hydrological pathways involved in producing stream discharge. Calls for geochemically based catchment models to include accurate hydrological structures [e.g., *Hooper et al.*, 1990; *Rice and Hornberger*, 1998] have bolstered this assertion and have emphasized the need for a rational, nonempirical approach for the identification of the significant sources of stream discharge and the assignment of chemical compositions to these individual components. Relationships derived from the integration of modeled hydrological processes with observed stream water chemistry can provide valuable insight into the transport of dissolved materials in a catchment.

Geochemical hydrograph separations, which are based upon the principle that water can pick up a unique chemical signature depending upon its source area, are used to determine the relative amounts of stream water that derive from different flow pathways. Applications of this technique often considered flow through two pathways, the surface and groundwater com-

ponents of discharge [*Pinder and Jones*, 1969; *Hooper and Shoemaker*, 1986; *Wels et al.*, 1991]. Evidence that more than two separate pathways must contribute to discharge was presented by *Christopherson et al.* [1990] for the Plynlimon catchment in Wales and the Birkenes catchment in Sweden. End-member mixing analysis (EMMA) diagrams indicated that the stream water chemistry was not simply an intermediary between two end-members but was instead a combination of discharge from at least three sources. In another, more generalized approach, *Evans and Davies* [1998] demonstrated that the episodic concentration-discharge (C-Q) hysteresis commonly observed for natural chemical tracers can preclude the use of only two components in mixing models. In accordance with these advances, recent chemical hydrograph separation studies such as those of *Ogunkoya and Jenkins* [1993], *Bazemore et al.* [1994], *DeWalle and Pionke* [1994], and *Rice and Hornberger* [1998] have employed three components of discharge. The surface component used in many hydrograph separation models is overland flow from variably saturated areas [*Dunne and Black*, 1970] and direct channel interception, runoff mechanisms that are active during the early portion of the storm hydrograph while precipitation is occurring. The overall contribution of these processes to storm flow discharge, however, is small for undisturbed catchments in humid, temperate regions, as isotopic studies have consistently shown [*Buttle*, 1994]. Therefore the two subsurface pathways must be conduits for the majority of the stream discharge. Groundwater or a “subsoil” [*Hendershot et al.*, 1992] equivalent is always used as a subsurface component. Water flowing through an intermediate soil zone, selectively referred to as the unsaturated

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[Hewlett and Hibbert, 1967], solum [Hendershot *et al.*, 1992], soil water [Mulholland, 1993], or hillslope [Hooper *et al.*, 1990] component is used as an additional subsurface end-member. In most cases the selection criteria for this third component are based upon geochemical considerations (e.g., fitting to vertices on EMMA diagrams) rather than direct field evidence of storm-initiated flow through this zone, although several mechanisms that may rapidly deliver water to streams while picking up the chemical signature associated with the shallow soil have been proposed and are summarized by Buttle [1994].

The use of a shallow subsurface component in catchment hydrochemical models assumes that this reservoir is distinct from the groundwater zone and is a significant contributor to stream discharge. The specific mechanism that allows for the rapid transport of water through this storm flow zone, however, often remains undefined. Observations in forested catchments have shown that above the permanent water table, in the macroporous shallow subsurface, perched water tables can form. This is true for the South Fork Brokenback Run (SFBR) catchment in Shenandoah National Park, Virginia (the site of the present study) [Scanlon *et al.*, 2000]. Saturated conditions in this storm flow zone are initiated when precipitation amounts are sufficient and coupled with wet antecedent conditions. At a similar hydrogeological setting at Oak Ridge, Tennessee, the rapid rise in the hydrograph and the variation in stream chemistry during and shortly following precipitation events has been attributed to preferential flow via transient, perched water tables in the macroporous upper soil profile [Mulholland *et al.*, 1990; Mulholland, 1993]. At this location, discharge collected in a subsurface weir has demonstrated that perched storm flow is capable of contributing to peak stream discharge [Wilson *et al.*, 1990]. Rapid solute transport through the preferential pathways in the A and B soil horizons, above the less permeable lower B and C horizons, has been observed in the Willamette Valley, Oregon [Hammermeister *et al.*, 1982a, 1982b]. Saturated flow in the shallow subsurface therefore can be regarded as a mechanism responsible for the rather large volumetric contributions of soil water to stream discharge predicted by many geochemical hydrograph separations.

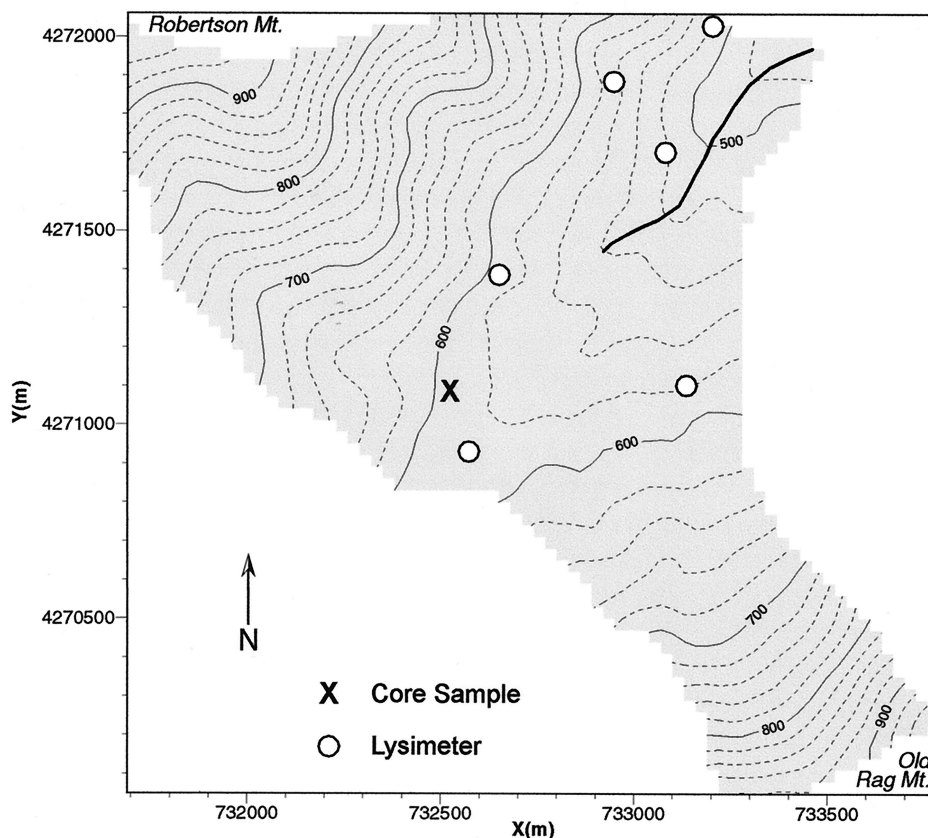
Hooper *et al.* [1990] report the success of coupled hydrological and geochemical models in reproducing the observed hydrographs and chemographs of reactive species, such as the Birkenes model [Christopherson and Wright, 1981; Christopherson *et al.*, 1982] and the PULSE model [Bergström *et al.*, 1985], but noted that the actual physical processes of the catchment were not captured. An alternative strategy for developing a linked hydrological-geochemical model utilizes well-documented, physically based concepts in conjunction with geochemical observations. TOPMODEL [Beven and Kirkby, 1979; Beven *et al.*, 1995] has previously been used to describe variations in stream water concentrations of acid-neutralizing capacity [Robson *et al.*, 1992] and dissolved organic carbon [Hornberger *et al.*, 1994], in which the conceptual model relied upon the use of one continuous water table where stream water concentrations are determined by the position of this water table relative to an upper and a lower soil zone. If below a certain horizon, the water has a groundwater signature, but as the water rises into the near-surface horizon, a fraction of it picks up the soil water signature. At the SFBR catchment, where the soil water component has been shown to arise, at least in part, from saturated flow disconnected from the permanent water table, this previously used conceptualization is not applicable. How might the inclusion of separate but linked

groundwater and storm flow reservoirs improve our understanding of catchment hydrochemical response?

Dissolved silica was chosen as a geochemical tracer for this study because of its prevalence in stream water from the weathering of the granitic bedrock of the SFBR catchment, its differential concentrations observed for water in the storm flow zone and the groundwater zone, and its near-zero concentration in precipitation. The dissolution of silica from the soil matrix can occur rather quickly [Kennedy, 1971], as many laboratory experiments have indicated. For example, McKeague and Cline [1963] found that the concentrations of dissolved silica increase rapidly after initial contact of water with soil, but after a day or two the concentration changed very slowly over time. Wels *et al.* [1991] conducted leaching experiments on soils and found that 80% of the silica dissolved over a 7-day experiment was released in less than 1 hour of contact time. The short time over which this tracer reaches an essentially steady state concentration has been used as justification for treating dissolved silica as a conservative tracer for hydrograph separations [Hooper and Shoemaker, 1986; Kennedy *et al.*, 1986; Maulé and Stein, 1990; Wels *et al.*, 1991; Hendershot *et al.*, 1992]. The concept of soil water maintaining a time-invariant silica "signature" throughout an event was scrutinized by Buttle and Peters [1997], who suggested that the re-packing of the soils by Wels *et al.* [1991] in their laboratory experiments was responsible for the observed rapid reactions. They point out that field soils contain structural voids, such as macropores, which may allow a portion of the event water to be transmitted to streams with limited contact with the soil. Although concentrations of silica in lysimeters were shown to remain constant over the course of an event, an observation also reported by Hendershot *et al.* [1992], Buttle and Peters [1997] used flow sampled from hillslope trenches to demonstrate that some dilution does occur during this time. Another observation was the presence of lower dissolved silica levels in base flow following a storm event compared with before the event, suggesting a time-varying signature for the groundwater zone.

Stream water C-Q relationships for storm events, during which the concentrations of dissolved constituents are most variable, can be used to interpret the hydrochemical response of a catchment. Underlying this method of analysis is the observation that different concentrations are frequently associated with equivalent discharges on the rising and receding limbs of storm hydrographs [Walling and Webb, 1986], a phenomenon commonly referred to as hysteresis. Instances in which rising limb concentrations are higher than those of the receding limb for like discharges have been attributed to the "flushing" of readily soluble material that accumulates during dry conditions in the upper soil [Walling and Foster, 1975]. Hooper *et al.* [1990] recognized that the flushing of unsaturated zone water with elevated concentrations of reactive tracers such as calcium and magnesium, for example, may contribute to hysteresis, but they noted that differences in concentrations and the timing of flow through multiple catchment pathways are far more important for producing this effect. EMMA considers this latter factor to be the sole contributor to hysteresis, and three-component mixing models have been shown to be capable of producing a wide range of C-Q looping patterns using fixed concentrations [Evans and Davies, 1998].

In this paper, a strategy for modeling the catchment hydrology along with stream chemistry is implemented with the following approach: (1) a dynamic hydrological model with a



**Figure 1.** Contour map of the South Fork Brokenback Run catchment. Also shown are the locations of the lysimeters and the location where the core was removed. The edges of the shaded area represents the watershed boundary.

structure consistent with the observed flow paths was developed and applied to the catchment; (2) representative concentrations of dissolved silica were assigned to water associated with these distinct flow paths; and (3) time series of discharge and stream water silica concentrations were produced by the model for three storms with differing antecedent conditions. From these results, C-Q relationships were developed and are compared with the observed stream hydrochemical behavior. Dissimilarities between the two are explored in the context of the suitability of using time-invariant concentrations for individual flow paths in hydrograph separations. This overall approach is essentially the inverse of traditional geochemical hydrograph separations: Rather than assuming prior knowledge of chemical signatures associated with the different flow pathways to the stream, we assumed knowledge of the flow apportioning from the individual reservoirs through the use of a physically based model such that the catchment-scale geochemical properties of these reservoirs could be investigated.

## 2. Site Description

The 237-ha SFBR catchment lies at the eastern margin of the Blue Ridge physiographic province in central Virginia and is part of the Rappahannock River basin. The steep slopes of Old Rag Mountain (996 m) and Robertson Mountain (1005 m) define the topographic boundary of the headwater catchment, which has an overall vertical relief of 523 m (Figure 1). Vegetation is typical of that in Shenandoah National Park, consist-

ing of second-growth mixed oak and hickory forest with lesser strands of other northern hardwoods, eastern hemlocks, and pine [Harrison, 1987]. The catchment is undeveloped with the exception of a National Park Service fire road, which roughly follows the course of the stream.

Precambrian Old Rag Granite, a coarse-grained porphyritic rock composed predominantly of microcline and quartz, underlies the entire catchment [Gathright, 1976]. Saprolite, the weathering product of the bedrock, has a thickness of 20 m along the side slopes but is absent along portions of the streambed and lower elevations, where bedrock is exposed [O'Brien *et al.*, 1993]. The physical and mineralogical characteristics of the saprolite are believed to be similar to that described by Pavich [1986] for the Piedmont physiographic province, where density increases with depth and clay assemblages are most abundant in the upper portions of the unit. The saprolite, which results from an isovolumetric weathering process in which between 20 and 60% of the mass is lost [Stolt *et al.*, 1992], is a potentially large reservoir for groundwater storage. The average thickness of the soil is approximately 1 m, and coarse colluvial deposits, consisting largely of granitic rocks and boulders, are predominant in the lower elevation and lower slope riparian area. A well-defined channel is established at the outlet and is present for approximately 150 m upstream. Gauging surveys have shown that the stream is gaining throughout its course, with several ephemeral surface inputs contributing to discharge.



Discharge and stream chemistry data were collected at this location by the U.S. Geological Survey (USGS) from 1983 through 1991. Subsequent to this period, the stream has migrated, bypassing the Parshall flume formerly used for the discharge measurements. Runoff ratio, the fraction of precipitation emerging from the catchment as discharge, ranged from 0.15 to 0.41 on an annual basis, with a mean of 0.30 for these 9 years of record. The average annual precipitation over this period was 1130 mm. The stream pH was reported to have ranged from 6.7 to 8.0, and the mean volume-weighted stream concentration of  $\text{SiO}_2$  was 9.31 mg/L [O'Brien *et al.*, 1997]. A groundwater well located on a hillslope near the upper reaches of the stream was sampled on an approximately monthly basis from 1984 to 1992 and had an average concentration of 10.57 mg/L ( $n = 80$  and standard deviation of 1.26).

### 3. Methods

#### 3.1. Field Methods

Stream stage was measured with a pressure transducer placed inside a stilling well at the catchment outlet. A downstream control, constructed of rock fragments collected in the stream bed, maintained subcritical flow at the point of measurement under most conditions. Routine dilution gauging was used to establish a stage-discharge relationship, and hourly averages of stream discharge were then determined. A tipping-bucket rain gauge was installed in a clearing 10 m from the catchment outlet. Temperature and humidity were measured at 15-min intervals, and the average daily temperature was used in the Hamon [1961] method for estimating potential evapotranspiration. A stage-actuated ISCO Model 3700 sampler was placed at the catchment outlet to take up to twenty-four 250-mL samples at 1-hour intervals when triggered by a storm event. Grab samples were taken periodically over a range of flow conditions.

#### 3.2. Laboratory Methods

To gain an understanding of how silica availability varies with depth at the SFBR catchment, batch experiments were conducted in which distilled water was mixed with regolith samples at a solid-to-solution (weight/weight) ratio of 1:100. Samples were obtained from a drill core that was held in dry storage for 15 years at the USGS offices in Reston, Virginia. The core was removed from SFBR catchment during the installation of the groundwater well (see section 2 for well data). Portions of the core corresponding to depths of 0.3, 0.5, 1.8, 5.2, 8.8, 12.5, 20.1, and 23.8 m below the surface were selected, and consolidated samples were ground by mortar and pestle to ensure that all samples had a similar granular texture. The regolith samples were added to beakers containing distilled water, and the solutions were continually mixed on a shaker table over the course of a 21-day period.

Analyses of dissolved silica concentrations for the batch experiment and stream water samples were performed at the Shenandoah Watershed Study laboratory at the University of Virginia using molybdenum blue colorimetry. Prior to analysis, samples were filtered at  $0.45 \mu\text{m}$  to remove particulate matter. Mineralogical analysis of the core, using X-ray diffraction, was performed by the USGS.

#### 3.3. Modeling Methods

A Matlab® version of TOPMODEL was developed and modified to include a second subsurface state variable repre-

senting the storm flow zone reservoir [Scanlon *et al.*, 2000]. Further additions to the model included the calculation of vertical recharge from the storm flow zone to the lower groundwater zone and the determination of a variable source area for overland runoff based on the interaction of both of these reservoirs. Following TOPMODEL procedure, the amount of water in each zone is quantified in terms of deficits. For instance, a local saturation deficit,  $S$ , is expressed as

$$S = \theta_n z_{wt}, \quad (1)$$

where  $\theta_n$  is the drainable porosity and  $z_{wt}$  is the depth to the water table. The average subsurface storm flow saturation deficit for the catchment  $\bar{S}_{sf}$  is reduced by inflow from the unsaturated zone,  $Q_{uz}$ , and is increased by discharge to the stream,  $Q_{sf}$ , and recharge to the groundwater zone,  $Q_v$ . Therefore, over a simulation time step  $\Delta t$  the change in the average stormflow saturation deficit for the catchment is

$$\frac{\Delta \bar{S}_{sf}}{\Delta t} = -Q_{uz} + Q_{sf} + Q_v. \quad (2)$$

Typically, TOPMODEL computes discharge from a subsurface reservoir as a function of average saturation deficit following the generalized form

$$Q = Q_0 \exp(-\bar{S}/m), \quad (3)$$

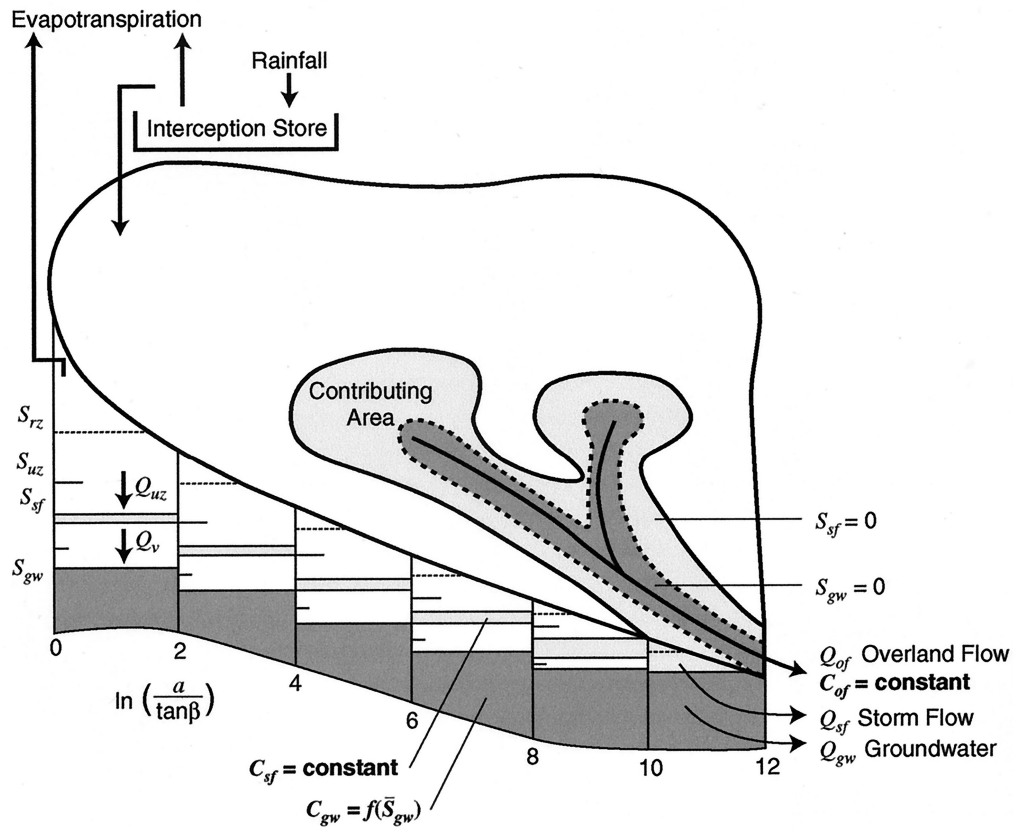
where  $Q_0$  and  $m$  are model parameters based on the catchment soil hydraulic properties and topography [Beven and Wood, 1983; Wolock, 1993]. As presented by Ambrose *et al.* [1996], (3) is applicable when saturated hydraulic conductivity decreases exponentially with depth and accordingly when the discharge recession is a first-order hyperbolic function of time. Scanlon *et al.* [2000] used hydrograph recession analyses to determine that (3) is appropriate for the groundwater zone but does not adequately describe the discharge behavior of the storm flow zone at the SFBR catchment. Instead, a TOPMODEL configuration in which hydraulic conductivity is uniform in this macroporous upper zone was shown to more accurately define  $Q_{sf}$ , and an alternative expression for (3) was used. The topographic index used for the storm flow zone is  $a/\tan \beta$  [Ambrose *et al.*, 1996], where  $a$  is the catchment contributing area per unit contour and  $\beta$  is the local slope, an adjusted form of the traditional  $\ln(a/\tan \beta)$  used for the groundwater zone in this application and in most other TOPMODEL applications.

Vertical recharge from the storm flow zone to the groundwater zone is approximated as a linear function of the local saturation deficit. The groundwater recession characteristics do conform well with (3) during periods in which recharge is inactive [Scanlon *et al.*, 2000], so the change in the groundwater storage deficit over a simulation time step is calculated by

$$\frac{\Delta \bar{S}_{gw}}{\Delta t} = -Q_v + Q_{0gw} \exp(-\bar{S}_{gw}/m_{gw}), \quad (4)$$

where  $m_{gw}$  is determined from hydrograph analysis [Scanlon *et al.*, 2000] and  $Q_{0gw}$  is analogous to  $Q_0$  in (3).

A mixing model was used to reconstruct a time series of stream silica concentrations using the three flow components of the modified TOPMODEL. Constant or variable dissolved silica concentration "signatures" were applied to each of the



**Figure 2.** Conceptual diagram of the modified TOPMODEL, including concentrations assigned to overland flow (constant), storm flow (constant), and groundwater (variable).

separate components of discharge: overland flow ( $Q_{of}$ ), sub-surface storm flow ( $Q_{sf}$ ), and groundwater ( $Q_{gw}$ ) (Figure 2). Stream water concentrations of dissolved silica ( $C_T$ ) were determined by the mixing equation:

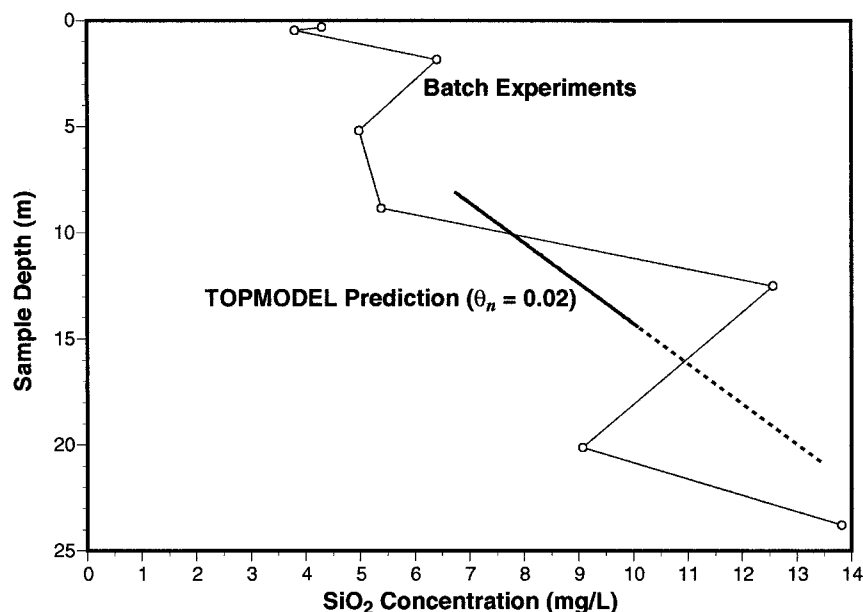
$$C_T = (Q_{of}C_{of} + Q_{sf}C_{sf} + Q_{gw}C_{gw}) / (Q_{of} + Q_{sf} + Q_{gw}), \quad (5)$$

where  $C_{of}$ ,  $C_{sf}$ , and  $C_{gw}$  refer to the dissolved silica concentrations of water emerging from the individual pathways. Discharge components were quantified by calibrating the modified TOPMODEL to match the observed hydrograph along with the timing of storm flow zone depletion, based upon hydrograph transform analysis [Scanlon *et al.*, 2000]. With "known" volumetric inputs from the three components of the hydrograph, solving for  $C_T$  requires knowledge of the silica concentrations associated with each of these components.

The value assigned to  $C_{sf}$  is the average dissolved silica concentration of 41 soil water samples collected in six tension lysimeters at the SFBR catchment during a period from April to October 1996 by Greene [1997]. The six lysimeters, which extend to depths of approximately 0.4 m below the surface, are all greater than 5 m from the stream (samples removed from lysimeters in the perennially saturated riparian area within 5 m of the stream showed higher levels of dissolved silica, probably from mixing with groundwater, and were not considered to be representative of storm flow zone concentrations). Soil water collected in the lysimeters was drawn through a porous ceramic cup, which removed some particulate matter, and these samples were not filtered before chemical analysis. The concentration of dissolved silica in overland flow,  $C_{of}$ , is difficult to

resolve from direct field measurements. This issue has been recognized in previous studies, and different approaches have been taken. Maulé and Stein [1990] assumed that water flowing over the catchment surface maintains a near-zero concentration of this geochemical tracer, identical to that of precipitation, while Wels *et al.* [1991] used an intermediate value between precipitation and soil water from the uppermost layer. In accordance with the rapid reactions between soil and water reported by Kennedy [1971], an approach similar to the latter study was decided upon for the present study in which the average value of throughfall and soil water was assigned to  $C_{of}$ .

During periods of base flow, groundwater is considered the sole contributor to stream discharge, and therefore dissolved silica concentrations in stream water should be that of  $C_{gw}$ . Because the modified TOPMODEL simulates the quantitative inputs of discharge from each of the three pathways, periods of base flow can thus be estimated. A simulation was performed for hours 360 through 7100 of water year 1998 (October 15, 1997, to June 23, 1998) to identify the observed dissolved silica concentrations in stream water that corresponded to conditions in which groundwater contributed greater than 98% of the total discharge. From this a relationship between  $\bar{S}_{gw}$ , the average groundwater storage deficit for the catchment, and  $C_{gw}$  was ascertained. TOPMODEL simulations were then undertaken for three different antecedent base flow conditions, using the concentrations assigned to the separate components, to predict time series of silica concentrations in stream water for individual storms.



**Figure 3.** Dissolved silica concentrations reached by mixing core samples, removed from various depths in the catchment subsurface, with distilled water for 21 days. The TOPMODEL prediction over the observed range of groundwater table fluctuations (solid line) is shown and is extended (dashed line).

## 4. Results

### 4.1. Mixing Experiment Results

The laboratory batch experiments provided an estimation of the dissolved silica “signature” picked up by the interstitial water within the subsurface, given sufficient contact time with the aquifer matrix material. The well-mixed solutions were measured at the end of the 21-day experiment. Variation in concentration with depth for a particular location in the catchment shows that water flowing through deeper sections of the groundwater reservoir has a potential to reach higher concentrations of dissolved silica than water that flows through the upper levels of this zone (Figure 3).

Two of the core samples were removed from depths of less than 2 m, the region in which shallow subsurface storm flow has been shown to be active [Scanlon *et al.*, 2000], and were found to have an average concentration of 4.84 mg/L. In comparison, a higher average concentration of 6.59 mg/L (standard deviation of 1.67) was found for the 41 lysimeter samples removed from the storm flow zone. This latter value was chosen to be representative of  $C_{sf}$  because it accounts for a more widespread sampling in space (see Figure 1) and time. As a first-order approximation, a value of 3.3 mg/L was selected for  $C_{of}$ , midway between the range of throughfall, 0.05 mg/L [Greene, 1997], and  $C_{sf}$ .

### 4.2. Dissolved Silica Variations in Groundwater

The modified TOPMODEL was parameterized and calibrated to match the features of the observed hydrograph [Scanlon *et al.*, 2000] for a period extending from hours 360 to 7100 of water year 1998 (Figure 4). Given the results of the batch experiment, we expected an increase in stream water silica concentration as the groundwater table dropped. Dissolved silica concentrations for flow conditions in which groundwater contributed to >98% of discharge were selected and plotted as a function of the calculated groundwater storage

deficit,  $\bar{S}_{gw}$  (Figure 5). A linear approximation to this trend reveals

$$C_{gw} = 26.34\bar{S}_{gw} + 3.52 \quad R^2 = 0.94, \quad (6)$$

where  $C_{gw}$  is the concentration of dissolved silica in the total groundwater output in mg/L. The variation of  $C_{gw}$  with  $\bar{S}_{gw}$  implies that the local concentrations of dissolved silica within the groundwater column,  $C_i$ , vary over the range of water table depths,  $z_{wt}$ . In order to convert (6) into an expression that describes this relationship, (1) must first be used to state this equation in terms of  $z_{wt}$ . Since  $C_{gw}$  results from the summation of groundwater inputs over a range of depths, the incremental concentrations,  $C_i$ , are related to  $C_{gw}$  according to

$$C_i(z_{wt}) \frac{dQ_{gw}(z_{wt})}{dz} = \frac{d}{dz} [C_{gw}(z_{wt})Q_{gw}(z_{wt})], \quad (7)$$

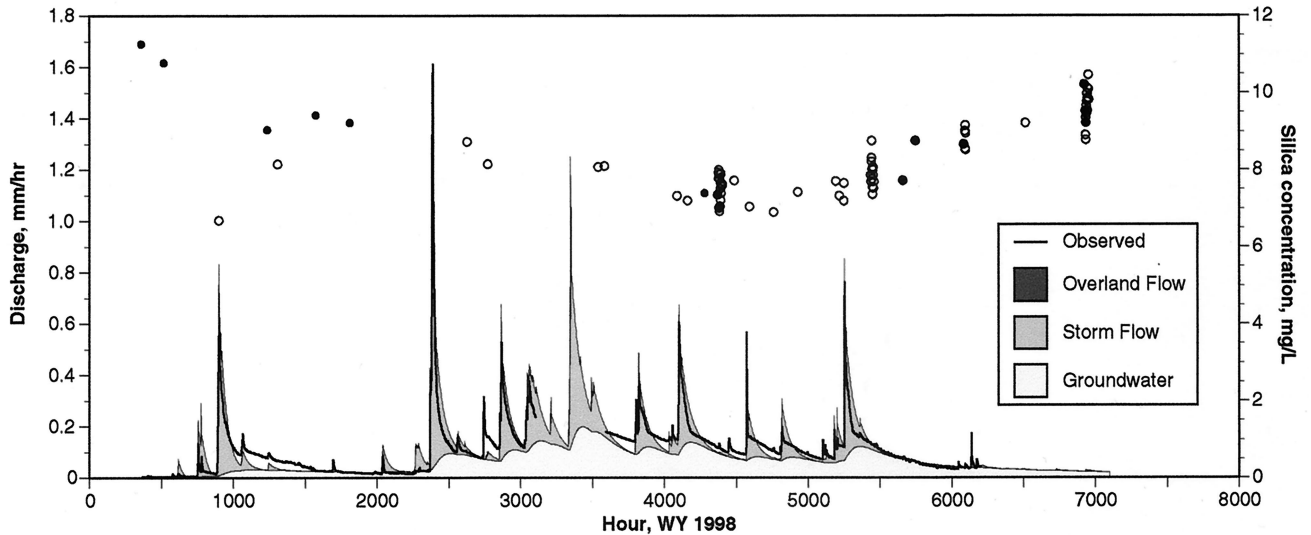
where

$$Q_{gw}(z_{wt}) = Q_{0gw} \exp -(z_{wt}\theta_n/m_{gw}). \quad (8)$$

From model calibration,  $Q_{0gw} = 0.0056$  m, and from hydrograph analysis,  $m_{gw} = 0.0401$  m [Scanlon *et al.*, 2000]. In the absence of detailed, depth-dependent information a constant value of 0.02 was used for  $\theta_n$ , which is appropriate for the clay-rich regolith [Johnson, 1967] at the SFBR catchment. When (8) is substituted into (7) and the resulting equation is differentiated, this reduces to

$$\begin{aligned} C_i(z_{wt}) &= 26.34\theta_n z_{wt} - 26.34m_{gw} + 3.52 \\ &= 0.527z_{wt} + 2.46, \end{aligned} \quad (9)$$

which shows that over the range of water table fluctuations (8.0–14.5 m) and given the model assumptions, the concentration of dissolved silica within the pore spaces of the groundwater, on average, increases linearly with depth (Figure 3).



**Figure 4.** Time series of observed discharge and modeled components of discharge for hours 360 to 7100 of water year 1998. Circles represent observed stream water dissolved silica concentrations. Solid circles correspond to times in which groundwater accounts for  $>98\%$  of the total modeled discharge. Overland flow, simulated by the model on the rising limb of the hydrograph, is not readily observable in Figure 4 because of the compaction of the time series.

#### 4.3. Modeled C-Q Hysteresis

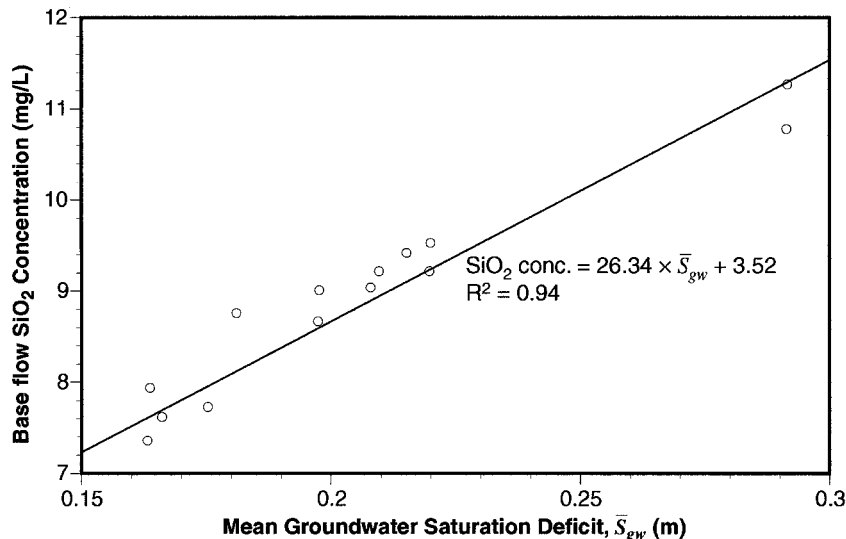
Simulations using the modified TOPMODEL, with  $m_{gw}$  set to 0.0401 m and with mixing concentrations set as described above, were undertaken in which modeled discharge was fitted to the observed hydrographs (initial conditions, storm flow zone recession slope, and a recharge parameter were reset) for a range of antecedent base flow conditions: low ( $5.30 \times 10^{-3}$  mm/h), intermediate ( $3.47 \times 10^{-2}$  mm/h), and high ( $1.44 \times 10^{-1}$  mm/h). Chemographs were simulated for each of these three events, and these data were also plotted in the form of C-Q diagrams (Figure 6). Model results for the low base flow event showed no overland flow, with slight hysteresis in the C-Q plot because the receding limb was composed of a greater percentage of groundwater (and less soil water) than the rising

limb at equal discharges. Overland flow induced a more pronounced effect upon the C-Q hysteresis for the wetter antecedent conditions (Figures 6b and 6c), a feature that was augmented by greater rises in the groundwater table during the course of these storms. In all three cases the C-Q paths display counterclockwise rotations.

## 5. Discussion

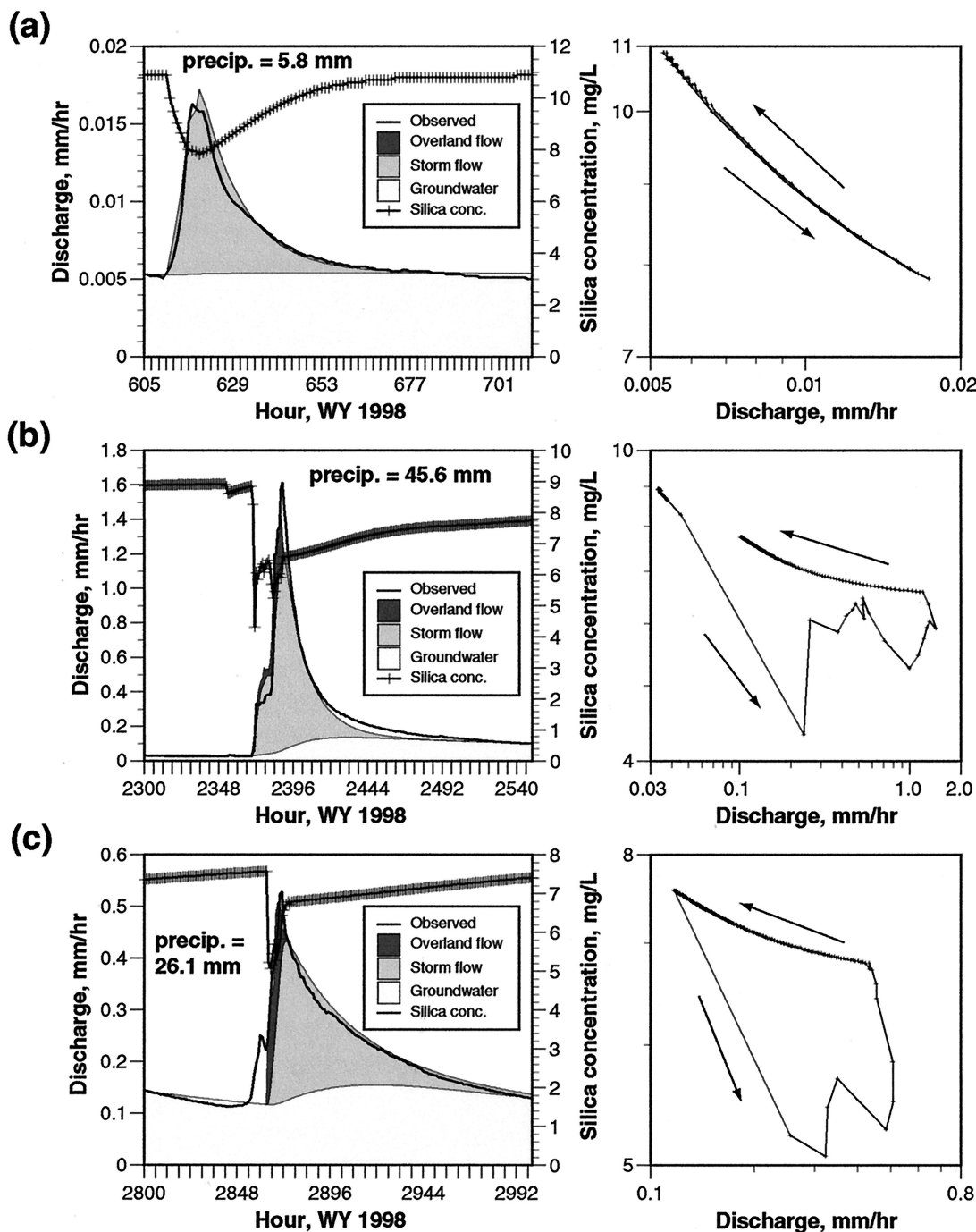
### 5.1. Groundwater Dissolved Silica Concentrations

One of the primary assumptions of hydrograph separations is that the chemical concentrations assigned to the discharge sources remain constant over the period of analysis [Pilgrim *et al.*, 1979; Robson and Neal, 1990; Buttle and Peters, 1997]. From



**Figure 5.** Dissolved silica concentration in stream water as a function of mean groundwater saturation deficit for conditions in which total stream discharge is composed of  $>98\%$   $Q_{gw}$ .





**Figure 6.** (left) Time series of observed discharge, modeled discharge components, and modeled dissolved silica concentrations, with (right) concentration-discharge diagrams for events with (a) low, (b) intermediate, and (c) high antecedent base flow conditions.

the relationship presented in Figure 5, it is evident that this assumption does not hold true for groundwater discharge as represented in our model of the SFBR catchment. Indeed, seasonal variations in dissolved silica concentrations in base flow have been noted in nearby catchments [Rice and Bricker, 1995; Rice and Hornberger, 1998] in which the differential availability of silicate minerals for weathering in the regolith and the bedrock, along with the difference in residence time for water flowing through these zones, have been hypothesized to control the bulk groundwater silica concentrations [Rice and

Bricker, 1995]. Short-term fluctuations in the level of the permanent water table are equally likely to cause variability in the groundwater dissolved silica "signature."

The batch experiments, using regolith samples removed from various levels of the subsurface at a single location within the catchment, provide an estimate of dissolved silica concentrations that pore water may reach given sufficient contact time. The depth dependency of silica concentrations from the batch experiments, as shown in Figure 2, is considered to reflect the subsurface mineralogy. The TOPMODEL-derived



relationship between incremental groundwater dissolved silica concentrations,  $C_i$ , and depth,  $z$ , conforms well with the batch experiment data (Figure 2), indicating that differential silica availability within the subsurface may largely control seasonal and subseasonal variations in  $C_{gw}$ . The steepest gradient in the batch experiment concentrations with respect to depth coincides with the levels over which the permanent water table fluctuates. Mineralogical analysis of the core sample removed from a depth of 8.8 m revealed an absence of potassium feldspar, the most abundant mineral in the Old Rag Granite [O'Brien *et al.*, 1997] and one of the most easily weathered of the bedrock components. The mineralogy at this level in the subsurface is dominated by quartz, which is relatively inert, and kaolinite and illite, which are indicative of general loss in silica mass [Righi and Meunier, 1995]. Below this the composition of the saprolite is more representative of the bedrock material, with K feldspar, plagioclase, and quartz all present. Parallel with the increase in saprolite bulk density with depth [Pavich, 1986] is an increase  $\text{SiO}_2$  mineral proportion [Gardner *et al.*, 1977]. At the Panola catchment, located in the Piedmont physiographic province of Georgia, this is reflected by an increase in the pore water silica concentrations as a function of depth in the 3-m-thick saprolitic zone [Stonestrom *et al.*, 1998]. One possible interpretation of the observed increase in  $C_i$  with depth is that, on average, the lower saprolite has more silicate minerals available for weathering, while much of the dissolvable silica in the upper portions of the saprolite has previously been removed.

## 5.2. Role of Residence Time in Groundwater Dissolved Silica Concentrations

The role of groundwater residence time in controlling dissolved silica concentrations in base flow is often difficult to characterize beyond a qualitative sense because of uncertainties associated with dissolution kinetics, the difficulty of reproducing field conditions in laboratory experiments, and the large timescales involved in the reactions. By expanding upon TOPMODEL concepts and by incorporating stream chemistry data from the SFBR catchment, however, a relationship between residence time and groundwater dissolved silica concentration can be developed. If flow through a groundwater zone is considered as a first approximation to not mix vertically, the mean residence time,  $T_r$ , of water reaching the stream from an average depth below the catchment surface,  $z$ , can be calculated by

$$T_r = \frac{\text{volume}}{\text{flux}} = - \left[ \frac{d}{dz} Q_{0_{gw}} \exp \left( - (z/\theta_{m_{gw}}) \right) \right]^{-1}, \quad (10)$$

where the differential equation represents the groundwater discharge (flux) as a function of storage (volume). After solving (10) and combining with (9), an equation for the pore water silica concentration as a function of residence time can be expressed as

$$C_i = 0.527 \left[ \frac{m_{gw}}{\theta_n} \left( \ln T_r - \ln \frac{m_{gw}}{\theta_n Q_{0_{gw}}} \right) \right] + 2.46. \quad (11)$$

This relationship, shown as Figure 7 for the region in the subsurface over which the water table fluctuates during the simulation period, reveals a more rapid increase in dissolved silica levels during earlier periods of contact with the regolith than during later periods. No steady state concentration is implied from (11) as  $T_r \rightarrow \infty$ , but this equation is applicable

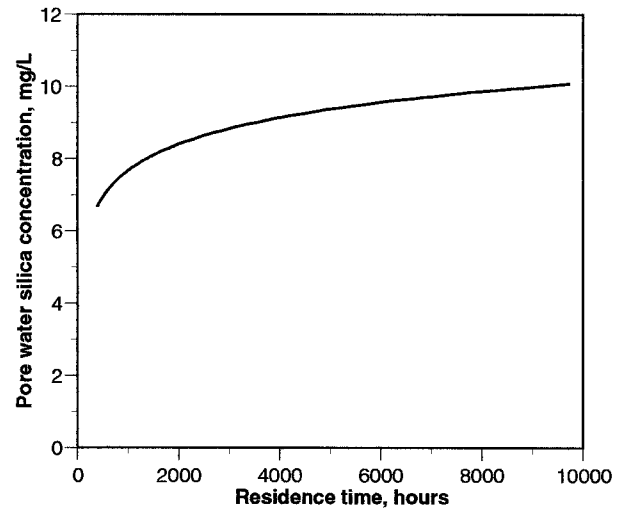


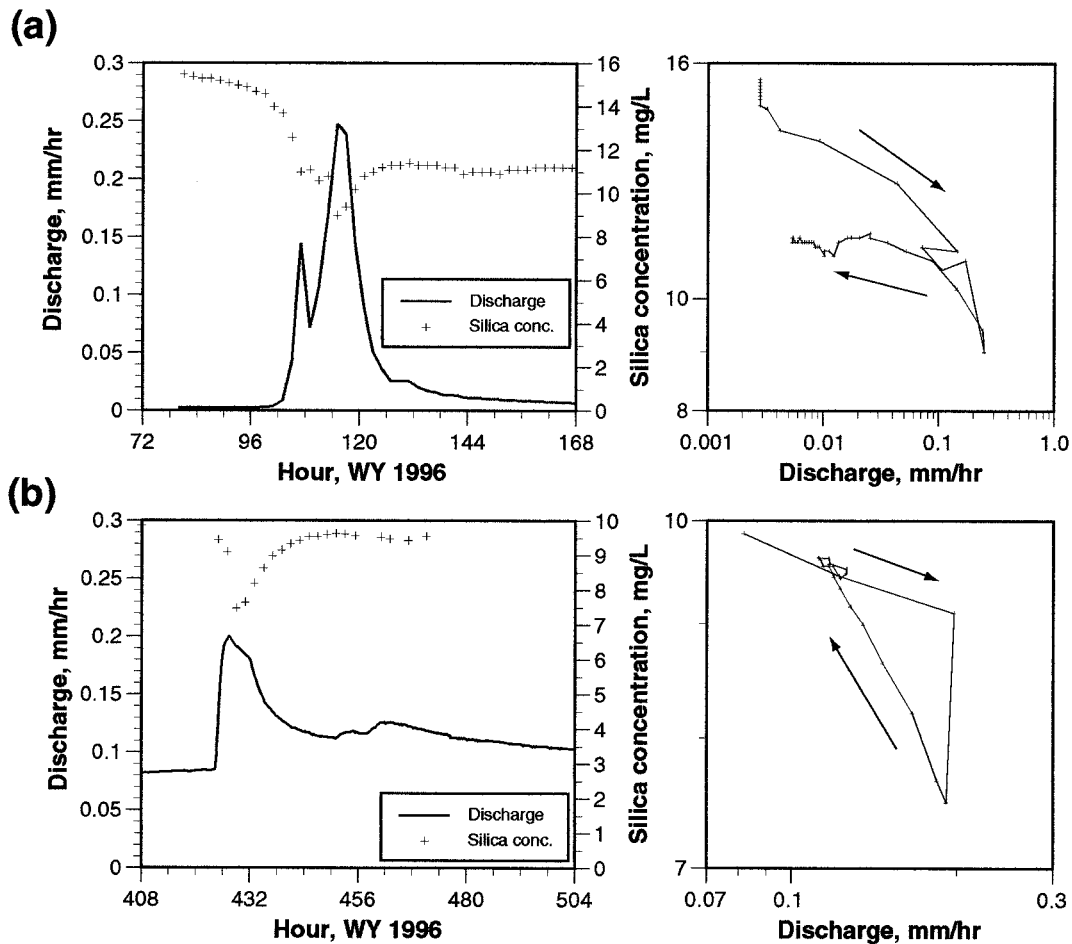
Figure 7. Dissolved silica concentration as a function of residence time calculated by TOPMODEL.

only when  $0.16 \text{ m} \leq \bar{S}_{gw} \leq 0.29 \text{ m}$  ( $387 \text{ hours} \leq T_r \leq 9743 \text{ hours}$ ), within bounds of the data presented in Figure 5. Given that pH, surface temperature, and vegetation do not have a significant influence on silica concentrations in stream water [Davis, 1964], regolith mineralogy and contact time are believed to be the two most likely factors in controlling  $C_{gw}$ . It is obvious from the variable concentrations with depth found in the batch experiments, along with the mineralogical differences in soil cores revealed by mineralogical analysis, that the regolith is heterogeneous with respect to the availability of silica for water flowing through different portions of the groundwater zone. Therefore attributing variations in  $C_{gw}$  to residence time alone, as in (11), disregards this important observation.

## 5.3. Modeled Versus Observed C-Q Hysteresis

With  $C_{gw}$  a function of  $\bar{S}_{gw}$ , simulations show that the prestorm flow levels of dissolved silica are higher than those following the storm flow recession. This feature is most evident in Figure 6b, in which 0.12 m of precipitation associated with this storm results in a significant rise in the groundwater table. If the prestorm value of  $C_{gw}$  were used in a traditional fixed end-member geochemical hydrograph separation, as is often done, this would result in a progressive underestimation of the groundwater discharge compared with that derived from a separation technique that accounts for a time-variant  $C_{gw}$ . Measurements by Greene [1997] at the SFBR catchment in water year 1996 confirm a discernible pattern of poststorm reduction in  $C_{gw}$  (Figure 8a), as captured by the model.

Insight into the linked hydrological and geochemical processes that take place during storm events may be attained by C-Q diagram analysis, an improvement over simple comparisons between time series of dissolved silica concentrations. Because  $Q_{gw}$  and  $C_{gw}$  are variable, slight hysteresis in the C-Q path can occur even under dry antecedent conditions when saturation excess overland flow is not an operative mechanism and changes in groundwater levels are minimal (Figure 6a). Under wetter antecedent conditions, overland flow is active during the rising limb of the storm hydrograph, and this accentuates the hysteretic effect (Figures 6b and 6c). The shape and counterclockwise rotation of the modeled C-Q paths cor-



**Figure 8.** (left) Time series of observed discharge and dissolved silica concentrations with (right) C-Q diagrams for water year 1996 data [from Greene, 1997]: (a) from 72–168 hours and (b) 408–504 hours.

respond to the *Evans and Davies* [1998] case in which  $C_{gw} > C_{sf} > C_{of}$ , consistent with the concentrations assigned to the components in this study. However, the C-Q paths from the observed stream discharge and chemistry exhibit a clockwise rotation (Figure 8), corresponding to the case in which  $C_{gw} > C_{of} > C_{sf}$ . By assigning a higher dissolved silica concentration to the overland flow than the water that flows through the shallow subsurface soil, the model can reproduce the shape of the observed C-Q path. The reasonableness of  $C_{of} > C_{sf}$  is questionable, however, considering the low silica concentrations associated with throughfall and the organic soil horizon, along with the short contact time between overland flow and the catchment surface.

#### 5.4. Possibility of Storm Flow Zone Flushing

An alternative explanation of the observed results requires (1) that  $C_{of}$  remain less than  $C_{sf}$  but greater than the ad hoc 50-50 mixture of throughfall and the soil zone signature used in the model simulations and (2) that  $C_{sf}$  decline over the course of a storm as the soil water is flushed out and more dilute water is added to the storm flow zone. *Buttle and Peters* [1997] report field evidence of this decline in  $C_{sf}$  during an event and point out that this undermines the assumption of rapid equilibrium reactions underlying many geochemical hydrograph separations. For the three modeled events (Figure 6) the storm flow zone contributes to discharge over a period of 2–5 days, during

which time the percentage of  $Q_{sf}$  that is preevent water, or water previously held in the unsaturated zone in contact with the soil for a long period of time, steadily decreases. Event water that reaches the stream via the storm flow zone may not have time to reach a steady state concentration with respect to the soil water silica during this period. Flushing mechanisms have been proposed to account for the mobilization of other constituents that accumulate at high concentrations in the unsaturated zone, including dissolved organic carbon [*Hornberger et al.*, 1994; *Boyer et al.*, 1997], dissolved organic nitrogen [*Creed and Band*, 1998], and sulfate [*Shanley and Peters*, 1993; *Steele and Buttle*, 1994]. The behavior of dissolved silica differs from these in that the dissolution reactions are thought to occur rapidly, allowing the event water to pick up a signature approaching that of the unsaturated zone water, thereby dampening the effect of hysteresis caused by the mixing of these waters. One possible way to quantify this effect in the model would be to use a variation of the approach taken by *Duffy and Cusumano* [1998], in which the time series of  $C_{sf}$  is influenced by the mixing of event water with ambient storm flow zone water and is controlled in part by ratio of the residence time for dissolved silica and the hydraulic relaxation time of the storm flow zone reservoir.

By applying a forward approach of modeling the components of discharge, the catchment-scale hydrochemical behavior of dissolved silica, the natural tracer used in this particular

study, could be further defined. During base flow conditions the stream water concentrations of dissolved silica were shown to be dependent upon the modeled groundwater levels, and on the basis of the modified TOPMODEL assumptions the dissolved silica concentrations in the groundwater varied with depth in qualitative agreement with a concentration profile derived from laboratory mixing experiments using a core that was removed from the catchment. Finally, the inability of the model to reproduce the observed C-Q hysteresis suggests that water with high concentrations of dissolved silica may be flushed from the storm flow zone as this zone becomes initially saturated during rainfall events. If the geochemical signatures associated with hydrological flow paths do vary in time, it follows that flow components cannot be unambiguously resolved using chemical and (or) isotopic measurements alone [Rice and Hornberger, 1998]. Just as the application of geochemical and isotopic hydrograph separation techniques has shaped our understanding of catchment hydrological processes, hydrological modeling can likewise be used to refine our understanding of geochemical transport in natural systems.

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